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DEVELOPMENT OF ADVANCED CONCEPTS FOR
IMPROVED HEAVY WATER PRODUCTION TECHNOLOGY

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I. Introduction

Research into deuterium-from-protium isotope separation via both metal hydride chromatography and CO₂ laser multiple-photon dissociation (MPD) of trifluoromethane (CDF₃/CHF₃) continued during the last reporting period. Several new classes of alloy compositions, including Mg-rare earth, NiTi_x, and [Ca+Ce,Zr,Ti]₈-Ni₄Cu compounds, were evaluated for chromatographic isotope separation; no tested alloy exhibited properties suitable for commercial deuterium separation. For deuterium separation by MPD of CDF₃, construction of a CO₂ laser system was completed that is capable of delivering either 2nsec short pulses at a single wavelength or 200nsec long pulses simultaneously at two different laser frequencies. The wavelength dependence of single-line multiple-photon dissociation probability of CDF₃ was measured, and is reported here. Deuterium separation by CO₂ laser photolysis of CDF₃/CHF₃ near 10.3 μ using \sim 2 nsec pulses still appears to be a commercially viable process for heavy water production.

II. Metal Hydride Chromatographic Deuterium Isotope Separation

A number of new alloy compositions were evaluated for suitability in the separation of hydrogen isotopes. Alloys of composition AMg_2 where A is one or more rare earths were evaluated. No compound was found with a high enough separation factor to be useful for commercial heavy water production. An alloy of $LaMg_2$ with seventy percent of the lanthanum replaced by calcium initially appeared promising as a lightweight hydride-forming alloy for hydrogen storage. After a few hydride-dehydride cycles, however, the alloy loses its ability to form a reversible hydride, apparently decomposing to form stable calcium hydride.

$NiTi$ and $NiTi_2$ were evaluated as a result of a German patent which claimed they formed a deuterium-free hydride. This claim was incorrect and neither alloy had a high enough separation factor to be useful.

A series of $Ca_{.8}Ni_4Cu$ based alloys were studied in which part of the calcium was replaced with cerium, zirconium or titanium. The alloy with 25 percent of the calcium replaced by cerium showed an improved equilibrium time and equilibrium pressure curve, and it will be used in future column experiments.

Column experiments were temporarily delayed during this reporting period due to the inability of a commercial supplier to provide calcium-nickel based alloys within the specified composition range. A new supplier with extensive experience with this type of alloy has been found. Sufficient quantities of $Ca_{.8}Ni_4Cu$ and $Ca_{.6}Ce_{.2}Ni_4Cu$ are now on hand to resume column experiments.

The reason for the failure of $Ca_{.8}Ni_4Cu$ filled columns to perform as well as expected¹ is still unknown. Air contamination during the filling of the column remains the most likely cause. This hypothesis will be tested as soon as new contamination free columns are completed.

Another series of column type experiments are planned with extremely short columns to study the re-equilibration time when the deuterium content of the gas stream is changed. If the gas flow rate is fast enough the column will be only one plate long and the true isotopic equilibration time can be determined. At present, this time is estimated from measurements of absorption and desorption curves.

III. Deuterium Separation by CO₂ Laser Photolysis of Trifluoromethane-d

Construction of the laser systems for CO₂ laser short pulse operation and dual wavelength operation were completed during the second half of the fiscal year.

Prior to commencing the study of two-wavelength IR photolysis in CDF₃, the wavelength dependence of single-wavelength CO₂ laser multiple-photon dissociation was measured using this assembled laser system. Preliminary measurements are presented in Figure 1, along with the low-fluence absorption profile. Data points were obtained by irradiation by ~ 25 pulses of $\sim 1.45 \pm 0.1$ J focused by a 1 m f.l. BaF₂ lens onto a 3.3 cm ID, 60 cm long cell containing a 40 mtorr CDF₃/20 torr Ar mixture. The fractional conversion from CDF₃ reactant to C₂F₄ product was determined by gas chromatography. The dissociation probability has a dual peak profile as does the absorption spectrum; however, the low energy peak near 970 cm⁻¹ is significantly higher, and perhaps broader, than the low energy peak, and is redshifted by at most ~ 5 cm⁻¹. Note that at P(20), 10.6 μ , a non-zero, though small, dissociation probability is still observed. This near-zero redshift is consistent with the extremely small anharmonic constant for the excited ν_5 mode in CDF₃. A redshift may still be observed in the two-wavelength IR photolysis study that is underway.

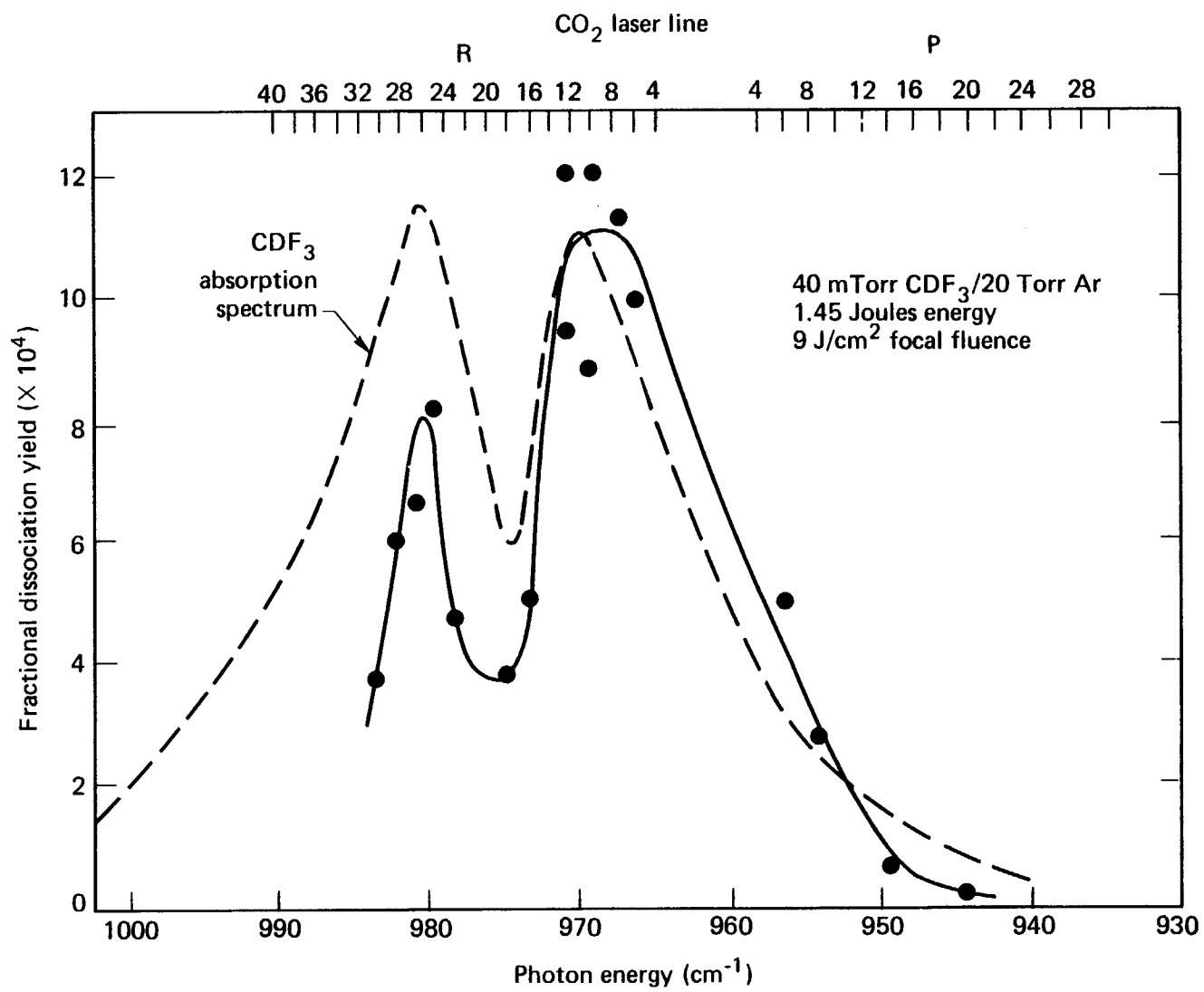
The pressure of CDF₃ was low enough in these runs to insure that essentially no CDF₃-CDF₃ collisions occurred during the 200 nsec long laser pulse. The 20 torr of argon was added to assure rotational relaxation during the pulse.

Assuming a uniform laser-beam transverse profile and the beam spot size as determined from burn patterns, the peak focal fluence was about 9 J/cm². However, at most wavelengths the transverse mode profile was quite structured. Consequently, due to the different mode structure and different laser energy (1.35—1.55 J/pulse) in trials at different wavelengths, the presented data has a ± 20 percent scatter. Using the integrated reaction yield, and assuming dissociation probability, $D(\phi)$, of the form:

$$D(\phi) = \left(\frac{\phi}{\phi_s}\right)^3 \quad \phi < \phi_s$$

$$= 1 \quad \phi \geq \phi_s$$

where ϕ is the local fluence and ϕ_s is the saturation fluence, ϕ_s is found to be ~ 16 J/cm² near 970 cm⁻¹. Beam inhomogeneities will increase this value to about 20 J/cm², in accord with our earlier observations.¹⁻³



During the coming quarter the CDF_3 dissociation probability will be measured under the condition of simultaneous excitation by pulsed CO_2 laser radiation at two different wavelengths. Product yields will be determined by gas chromatography and/or by measurement of the fluorescence intensity of the nascent DF photolysis product.

IV. References

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V. Patent Activity

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2. F. T. Aldridge, Chromatographic Hydrogen Isotope Separation, S-041-364, Filed May 22, 1979, allowed October, 1980; Canadian Patent Filed 1980.